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(54) Ultraviolet curable conformal coatings.

(57) A two package UV curable conformal coating has been developed which possesses low moisture permeability and good electrical properties and provides a cure for shadowing of components on a printed wiring board. The conformal coating is a mixture of Component (A) which is a mixture of (1) from 40 to 80% by weight, of a urethane having a free isocyanate group; (2) from 20 to 60%, by weight, of reactive acrylate diluents; (3) from 0 to 10% by weight of UV photoinitiators; and (4) from 0 to 10% by weight of additives; and Component (B) which is a mixture of (1) from 50 to 80% by weight of an acrylate-epoxy resin; (2) from 1 to 10% by weight of an acrylate-urethane oligomer; (3) from 10 to 94% by weight of reactive acrylate monomers; (4) from 0 to 10%, by weight, of UV photoinitiators; and (5) from 0 to 10% by weight of additives; with the proviso that the total weight percentage of said photoinitiators and additives respectively each not be less than 1 percent and not exceed 10 percent. Components A and B may be mixed in equal parts, by weight, or in a 1 to 2 part ratio, by weight.

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IMPROVEMENTS IN OR RELATING TO RESIN COMPOSITIONS CURABLE WITH ULTRAVIOLET LIGHT

Conformal coatings that are UV curable have the advantages that they can be cured rapidly (in seconds) with no volatile organic compounds being emitted, so they are well suited for an automated electronic assembly line. However, there is an inadequate cure due to shadowing by the components. U.S. Patents 4,424,252 and 4,668,713, for example, disclose a secondary cure mechanism to cure these shadow areas.

We have discovered an ultraviolet (UV) curable conformal coating possessing good electrical properties, low moisture permeability, good pot life and shadow cure capabilities. The UV curable conformal coating composition of the present invention is preferably applied by spray, dipping, and knife coating on a substrate such as printed wire or circuit boards.

Accordingly, the present invention resides in a UV curable composition characterized in that a mixture of Component (A) which is a mixture of (1) from 40 to 80% by weight, of a urethane having a free isocyanate group; (2) from 20 to 60% by weight, of reactive acrylate diluents; (3) from 0 to 10% by weight of UV photoinitiators; and (4) from 0 to 10% by weight of additives. Component (A) may optionally contain from 1 to 25% by weight of polyisocyanate monomers.

Component (B) is a mixture of (1) from 5 to 80% by weight of an acrylate-epoxy resin; (2) from 1 to 10% by weight of an acrylate-urethane oligomer; (3) from 10 to 94% by weight of reactive acrylate monomers; (4) from 0 to 10% by weight of UV photoinitiators; and (5) from 0 to 10% by weight of additives, with the proviso that the total percentage weight of the photoinitiators and additives respectively, each not be less than 1% and not exceed about 10 percent.

Component (B) may optionally contain from 5 to 80% by weight of epoxy resins; from 1 to 10% by weight of polyols; and/or from 5 to 80% by weight of an acrylate epoxy urethane.

The composition of the present invention is a two-part system and is compatible with in-line assembly. Specifically, the composition has a good adhesion, good electrical insulating properties, low moisture permeability, good thermal stability, and rapid cure times. The composition is particularly suited for curing even of shadow areas, i.e., areas hidden from the UV light source by the presence of electronic components.

The composition of the present invention may be applied by spray, dipping and knife coating, and cured by ultraviolet radiation in a very short time of less than about 2 to 4 seconds. The rapid curing of the composition of the present invention enables its use in automated printed wiring board assembly lines.

The UV curable composition of the present invention is a two package or component system. The first component is a mixture of a urethane having a free isocyanate group in reactive acrylate diluents. The second component contains resin blends of acrylate epoxy and acrylate urethane in reactive acrylate monomers. Photoinitiators and/or additives may be included in either or both components.

The components of the UV curable resin compositions of the present invention will now be described in detail as follows.

Component A

(1) Urethane having a free isocyanate group

The urethane may preferably be a urethane or an acrylate urethane. The urethane or acrylate urethane provides flexibility, toughness and hardness.

The urethane is obtained by reacting alcohols or polyols with one stoichiometric equivalent of excess polyisocyanates. The alcohols or polyols may be aliphatic, aromatic or mixtures thereof.

Examples of suitable alcohols include methanol, ethanol, butanol, hexanol, phenol, mixtures thereof and the like. The alcohols having more than four carbons in a straight chain are preferred for flexibility.

Examples of suitable low molecular weight polyols are butanediol, hexanediol, ethylene glycol, tetra ethylene glycol, dihydroxy ethyl quinone, glycerin, trimethylolpropane, tris-hydroxy-ethyl isocyanurate mixtures thereof and the like. The (poly)ethylene glycols are preferred for adhesion. The alcohols or polyols may also possess acrylate functional group for a fast UV cure.

Examples of suitable acrylate alcohols or polyols and more specifically preferred hydroxy acrylates, include 2-hydroxyethyl acrylate (HEA), 3-hydroxypropyl acrylate, 2-hydroxy methacrylate, hydroxyethyl-

beta-carboxyethyl acrylate, 3-hydroxypropyl methacrylate, hydroxyhexyl acrylate, hydroxyoctyl methacrylate, 2-hydroxypropyl acrylate, and 2-hydroxyethyl methacrylate. Di- and polyacrylates may also be used but they are not preferred as the resulting coatings may be too brittle. The preferred hydroxy acrylate is 2-hydroxyethyl acrylate because it is very reactive and results in a fast curing composition.

Polyisocyanates may be used to produce the free isocyanate group. The polyisocyanate may either be difunctional, but diisocyanates are more preferred.

Examples of suitable diisocyanates include:

- 4,4'-diisocyanato diphenyl 2,2-propane (4,4'-diphenyl-2,2-propane diisocyanate)
- 4,4'-diisocyanato diphenyl methane (4,4'-diphenylmethane diisocyanate)
- 4,4'-diisocyanato benzidine (4,4'-diphenyl diisocyanate)
- 4,4'-diisocyanato diphenyl sulfur (4,4'-diphenylsulfide diisocyanate)
- 4,4'-diisocyanato diphenyl sulfone (4,4'-diphenylsulfone diisocyanate)
- 4,4'-diisocyanato diphenyl ether (4,4'-diphenylether diisocyanate)
- 4,4'-diisocyanato diphenyl 1,1-cyclohexane (4,4'-diphenyl-1,1-cyclohexane diisocyanate)
- oxides of methyl- and of bis (meta-isocyanato-phenyl) phosphine (methyl and bis(meta-phenyl isocyanate) phosphine oxide)
- diisocyanato 1,5-naphthalene (1,5-naphthalene diisocyanate)
- meta-phenylene diisocyanate
- tolylene diisocyanate (tolylene diisocyanate or toluene diisocyanate)
- 3,3'-dimethyl diphenyl 4,4'-diisocyanate (dimethyl 3,3'-diisocyanato 4,4'-diphenylene)
- 3,3'-dimethoxy diphenyl 4,4'-diisocyanate (dimethoxy 3,3'-diisocyanato 4,4'-diphenylene)
- meta-xylylene diisocyanate
- para-xylylene diisocyanate
- 4,4'-dicyclohexylmethane diisocyanate (diisocyanato 4,4'-dicyclohexyl methane)
- hexamethylene diisocyanate
- dodecamethylene diisocyanate
- 2,11-dodecane diisocyanate (diisocyanato 2,11-dodecane)
- bis(para-phenylene isocyanate 1,3,4-oxadiazole) para-phenylene
- bis(para-phenylene isocyanate), 1,3,4-oxadiazole
- bis(meta-phenylene isocyanate), 1,3,4-oxadiazole
- bis(meta-phenylene isocyanate)4-phenyl 1,2,4-triazole
- bis (4-paraphenylene isocyanate thiazole 2-yl) metaphenylene
- (2-phenylene)5,4'-benzimidazole diisocyanate
- (2-phenylene)5,4'-benzoxazole diisocyanate
- (2-phenylene)6,4'-benzothiazole diisocyanate
- 2,5-bis(2-phenylene isocyanate benzimidazole-6-ene) 1,3,4-oxadiazole
- bis(para-phenylene isocyanate-2-benzimidazole-6-ene)
- bis(para-phenylene isocyanate-2-benzoxazole-6-ene)

The preferred diisocyanate is tolylene diisocyanate (TDI) because it is inexpensive and has been found to work well.

The preparation of the urethane having a free isocyanate group is conducted in the presence of an inhibitor (i.e., a free radical scavenger) such as naphthoquinone, phenanthraquinone, 2,6-di-tert-butyl-4-methyl phenol, benzoquinone, hydroquinone, or methylquinone to prevent the spontaneous polymerization of acrylic groups. At least 0.01% inhibitor (based on the total weight of the second resin) should be used. If less inhibitor is used, the oligomer may gel. However, more than 0.1% of the inhibitor should be avoided as the UV reactivity may then be low.

The reaction of the diisocyanate with the hydroxy acrylate proceeds readily at about 60°C for 1 hour. A proportion of 1 mole of diisocyanate to 1 mole of the hydroxy acrylate should be used so that the resulting urethane compound has a free isocyanate group.

It is preferred that the urethane having a free isocyanate group be present in an amount of about 40 to 80% by weight.

2) Reactive acrylate diluents

The acrylate diluents are used as reactive diluents to reduce the viscosity of resin and improve the storage stability of resin. The reactive acrylate diluents should possess good solvency characteristics for the urethane having a free isocyanate group. The reactive acrylate diluents should be free of active hydrogen,

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(i.e., hydroxy or amine groups), should have good solubility to resin, and low moisture permeability in the final cured coating. The acrylate monomers containing more than three acrylate functional groups should be avoided because they may cause the coating to be too brittle. Phenoxy ethyl acrylate (PEA) and hexanediol diacrylate (HDDA) are preferred acrylate diluents. However, any mono- or diacrylate monomers such as phenol ethoxylate monoacrylate tetraethylene glycol diacrylate (TEGDA), 2-2-ethoxy ethoxy ethyl acrylate, tripropyl glycol diacrylate and mixtures thereof may be used.

The reactive acrylate diluents are preferably present in an amount of 20 to 60% by weight.

3) UV photoinitiators

Also required in the composition is a photoinitiator. The photoinitiator is a compound that generates free radicals when exposed to ultraviolet light. The free radicals then initiate the free radical chain polymerization of the acrylate groups in the composition. Photoinitiators are well known to those skilled in the art. They are often mixtures of several different compounds and are frequently proprietary.

The photoinitiators suitable for use in the present invention include glyoxalate derivatives, benzoin ether derivatives, alpha-acryloxime ester derivatives, acetophenone derivatives, and ketone-amine combinations.

Examples of suitable photoinitiators include: isobutyl benzoin ether (V-10, a product of Stauffer Chemical), isopropyl benzoin ether, benzoin ethyl ether, benzoin methyl ether, 1-phenol-1,2-propane-dione-2-(O-ethoxycarbonyl) oxime, 2,2-dimethoxy-2-phenyl-acetophenone (IRG-651, a product of Ciba Geigy), benzyl hydroxy-cyclohexyl phenyl ketone, diethoxyacetophenone, 2-hydroxy-2-methyl-1-phenyl-propane-1-one, and methyphenyl glyoxalate (V-55, a product of Stauffer Chemical).

The ketone-amine combination is preferably a primary or secondary, aliphatic or aromatic amine and ketones which include benzophenone, 2-chlorothioxanthone, isopropyl thioxanthone, 2-methylthioxanthone, chlorine functional substituted benzophenone, halogen substituted alkyl-arylketones, wherein halogen is chlorine, bromine, or iodine.

The photoinitiator may be mixtures of the above-described suitable photoinitiators.

The UV photoinitiator may be present in either or both components. However, the total weight percentage of the photoinitiator in both components should not exceed 10 percent, by weight.

4) Additives

Additives modify certain properties of the compositions of the present invention such as flow, adhesion and fluorescence.

Suitable adhesion promoters may be present in amounts of from 0-1% by weight, and preferably from 0.01 to 0.1% by weight, of the total composition weight. Phosphate or mercaptan derivatives, such as acrylated mercaptan (EB19-6375, a product of Radcure, Inc.) or acrylated phosphate ester (EB-19-6170, a product of Radcure, Inc.) and mixtures thereof may be added to the adhesive composition.

Various other compounds may be included in the composition as desired including, for example, dyes or pigments that are, however, UV transparent for easy inspection in the assembly line and flow control agents for easy application and reduced moisture permeability. Suitable flow control agents include alkylphenol ethoxylate, alcohol ethoxylate, fluorohydrocarbons such as fluorinated alkyl alkoxylate and ether sulfate.

Additives may be present in either or both components. However, the total weight percentage of the additive in both components should not exceed about 10%. It is preferred that the additives be present in Component (B).

5) Polyisocyanate monomers

Polyisocyanate monomers are an optional ingredient in Component (A). The polyisocyanate monomers provide additional moisture cure capabilities. The polyisocyanate monomers may be either alkyl having a carbon length of 1 to 10 or an aromatic polyisocyanate. Aromatic polyisocyanates are preferred due to their high reactivity and good thermal stability. The polyisocyanate monomers should be compatible with other ingredients in the system and be in liquid form at room temperature. Suitable polyisocyanate monomers include toluene diisocyanate isomers, phenylene diisocyanate isomers, xylene diisocyanate isomers, and mixtures thereof. It is preferred that the isocyanate monomers be present in an amount of 1 to 25% by

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weight.

Component B

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The major ingredients of the Component (B) of the UV conformal coating composition are (1) from 5 to 80% by weight of an acrylate-epoxy resin; (2) from 1 to 10% by weight of an acrylate-urethane resin; (3) from 10 to 94% by weight of reactive acrylate monomers which include from 10-50% acrylate monomers containing hydroxy functional group, from 10-50% acrylate monomers having good solubility to resins such as phenoxy ethyl acrylate; from 10-50% acrylate monomers having low moisture permeability for final cured coating, and from 1-15% acrylate monomer containing ether linkage for good coating adhesion; (4) from 0 to 10% photoinitiators and (5) from 0 to 10% additives.

Acrylate epoxy and acrylate urethane are oligomers which provide the main characteristics of the coating such as moisture and chemical resistance, flexibility, adhesion, toughness and hardness.

Optionally, from 5-80% epoxy resin, from 1-10% polyol, and/or from 5-80% acrylate epoxy urethane resin may also be included in the composition. The secondary hydroxy group in the optional epoxy resin can react with free isocyanate in Component (A) of the two-component system. The epoxy resin also improves the adhesion of the coating. The polyol reacts with any residual free isocyanate from Component (A). The acrylate epoxy urethane resin improves the adhesion, hardness and toughness of coatings.

Each of the elements of Component B will be discussed in detail as follows:

1) Acrylate-epoxy resin

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The acrylate-epoxy oligomer or resin is related to the UV curable compositions described in U.S. Patent Specification No. 4,481,258, assigned to the assignee of this invention and herein incorporated by reference.

The acrylate-epoxy oligomer used in the UV curable adhesive composition of this invention is an unsaturated epoxy oligomer dissolved in a reactive acrylate diluent. The unsaturated epoxy oligomer is a compound having both ethylenic unsaturation and free epoxy groups, and a molecular weight of from 2000 to 5000. Oligomers having a lower molecular weight tend to form a bond that is too brittle, and oligomers having a higher molecular weight tend to make the composition too viscous. Acrylic unsaturation is preferred as it cures faster, but allylic or vinylic unsaturation may also be used.

An acrylate-epoxy oligomer, the preferred oligomer, can be made by acrylating an epoxy resin. For example, an epoxy resin can be acrylated in a two-step reaction. In the first step, a hydroxy acrylate, a compound having both acrylate groups and a single hydroxyl group, is reacted with an anhydride or a diacid to form an ester having a free carboxylic acid group and a free acrylate group. The reaction occurs between a carboxylic group of the diacid or anhydride, and a hydroxyl group of the hydroxy acrylate. Suitable hydroxy acrylates that can be used in this reaction have been described in Component (A).

Suitable anhydrides that may be used include trimellitic anhydride, maleic anhydride, methylbicyclo-[2.2.1] heptene-2,3-dicarboxylic anhydride, phthalic anhydride, methylnadic anhydride, and hexahydrophthalic anhydride. Di- or polyanhydrides can also be used but they are not preferred because they may cause the composition to gel. Suitable diacids that may be used include terephthalic acid, isophthalic acid, oxalic acid, adipic acid, and succinic acid. Trimellitic anhydride (TMA) and maleic anhydride (MA) are preferred because they give a composition having a longer pot life and better adhesion and better thermal stability.

The resulting ester is then reacted with an epoxy resin to form the acrylate-epoxy oligomer. The epoxy resin can have more than two epoxy groups, but diepoxides are preferred as more reactive polyepoxides may make the coating too brittle. The epoxy resin is preferably a bisphenol epoxy, such as bisphenol A epoxy resin, bisphenol F epoxy, a bisphenol S epoxy resin, or mixtures thereof, as these epoxy resins promote the best adhesion of the coating to the surface. Bisphenol A epoxy resin is the least expensive and provides an excellent bond on the substrate.

The epoxy resin should be soluble in a reactive diluent, and preferably a liquid acrylate which provides a liquid medium for the reactants. The reactive diluent reacts later and becomes part of the resin. Examples of suitable reactive diluents include phenoxyethyl acrylate (PEA) phenol ethoxylate monoacrylate, tetrahydrofurfuryl methacrylate, cyclohexyl methacrylate, n-hexyl methacrylate, 2-(2-ethoxyethoxy) ethyl acrylate and mixtures thereof. An inhibitor, such as benzoquinone, is included to deter reaction of the liquid

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acrylate during the epoxy resin-ester reaction. The preferred reactive diluent is phenoxy ethyl acrylate (PEA) because it possesses good solvency characteristics for the oligomer. Sufficient reactive diluent should be used to give the resin a workable viscosity; from 10 to 50% by resin weight of the reactive diluent is usually sufficient.

5 An epoxy catalyst, such as a tertiary amine, (e.g. triethanolamine (TEA)), may be used to promote the reaction of the ester and epoxy resin to form the oligomer. Generally, at least 0.01% (all percentages herein are by weight unless otherwise indicated) catalyst (based on the weight of the resin composition) is required, and more than 0.1% catalyst should be avoided as it makes the reaction difficult to control and may result in clouding.

10 The purpose of reacting the hydroxy acrylate with the anhydride or diacid is to produce an acrylate that will react with an epoxy group of an epoxy resin. Therefore, the hydroxy acrylate, the anhydride or diacid, and the epoxy resin should be used in such proportions that in the acrylate-epoxy oligomer all groups are reacted except for the acrylate group on the hydroxy acrylate and one epoxy group. The reaction proceeds with moderate heat at from 140 to 150° C and is finished when the acid number is less than 5.

15 Alternatively, the resin may comprise an acrylate-epoxy oligomer by reacting a hydroxy acrylate, as described hereinbefore, and maleic anhydride. The resulting ester is reacted with an epoxy such as a bisphenol epoxy and/or an epoxy novolac in a reactive diluent such as phenoxy ethyl acrylate (PEA) containing an inhibitor such as benzoquinone. More than about 10% novolac should be avoided to prevent gelling.

20 It is preferred that the acrylate-epoxy resin be present in an amount of from 5 to 80% by weight.

2) Acrylate-urethane oligomer

25 The second resin in the Component (B) is an acrylate urethane oligomer. This oligomer can be prepared by reacting a diisocyanate with a hydroxy acrylate first, then reacting further with caprolactam. Examples of suitable diisocyanates have been described in Component (A):

Suitable hydroxy acrylates can be selected from the hereinabove provided examples in Component (A). The preferred hydroxy acrylate is 2-hydroxyethyl acrylate because it results in a faster reaction. In this
30 reaction, an isocyanate group of the diisocyanate reacts with the hydroxyl group of the hydroxy acrylate to produce a urethane. This reaction is conducted in the presence of an inhibitor (i.e., a free radical scavenger) such as naphthoquinone, phenanthraquinone, 2,6-di-tert-butyl-4-methyl phenol, benzoquinone, hydroquinone, or methylquinone to prevent the spontaneous polymerization of acrylic groups. At least 0.01% inhibitor (based on the total weight of the resin) should be used. If less inhibitor is used, the oligomer
35 may gel. However, more than 0.1% of the inhibitor should be avoided as the UV reactivity may then be low.

The reaction of the diisocyanate with the hydroxy acrylate proceeds readily at about 60° C for 1 hour. A proportion of 1 mole of diisocyanate to 1 mole of the hydroxy acrylate should be used so that the resulting urethane compound has a free isocyanate group. That isocyanate group is then reacted with caprolactam to produce a urea linkage. The reaction with caprolactam can be performed at about 100° C until no
40 isocyanate peak is observed in an infrared absorption spectrometer. From 10 to about 50% by weight, based on the weight of the second resin, of an acrylate is then added as a diluent to make the oligomer less viscous. Suitable acrylate diluents may be found in the list provided hereinabove in Component (A), and PEA is again preferred. A description of the acrylate urethane resins can be found in U.S. Patent Specification 4,481,258 (herein incorporated by reference).

45 It is preferred that the acrylate urethane oligomer or resin be present in an amount of from 1 to 10%, by weight.

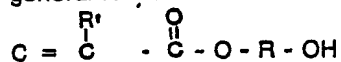
3) Reactive acrylate monomers

50 Reactive acrylate monomers are preferably present in an amount of from 10 to 94% by weight. The reactive acrylate monomers include a) acrylate monomers having a hydroxy functional group, b) resin soluble acrylate monomers, c) acrylate monomers having low moisture permeability, d) an acrylate having ether linkages and mixtures thereof.

a) Acrylate monomer having a hydroxy functional group

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Suitable acrylates having a hydroxy functional group have been described in Component (A). They have general formulations such as:



- 5 where R may be aromatic or aliphatic chain of 1 to 10 carbons and R' may be hydrogen or an alkyl group having 1 to 10 carbons. The acrylate monomer having a hydroxy group is preferably present in an amount of from 10 to 50% by weight.

10 b) Resin soluble acrylate monomers

Suitable resin soluble acrylate monomers include phenoxyethyl acrylate (PEA), phenol ethoxylate monoacrylate, tetrahydrofurfuryl methacrylate, n-hexyl methacrylate and mixtures thereof. The resin soluble acrylate monomer is preferably present in an amount of from 10 to 50% by weight.

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c) Acrylate monomers having low moisture permeability

- 20 Suitable acrylate monomers having low moisture permeability are preferably alkylene diacrylates having 1 to 10 carbons in the alkylene portion of the compound. Suitable examples include hexane diol diacrylate, ethylene glycol diacrylate, 1,3-butylene glycol diacrylate, 1,4-butanediol diacrylate and neopentyl glycol diacrylate and mixtures thereof. The acrylate monomer having low moisture permeability is preferably present in an amount of from 10 to 50% by weight.

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d) Acrylate monomers having ether linkages

- 30 Suitable acrylate monomers having ether linkages provide good adhesion and include ethyl glycol diacrylate (EGDA), tetraethyl glycol diacrylate (TEGDA), diethylene glycol diacrylate, ethoxylated bisphenol A diacrylate, tripropylene glycol diacrylate and mixtures thereof. The acrylate monomers having ether linkages are preferably present in an amount of from 1 to 15% by weight.

4) Photoinitiators

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Photoinitiators have been discussed above.

5) Additives

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Additives have been discussed above.

6) Epoxy resin

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- 50 An epoxy resin may be optionally added in an amount of from 5 to 80% by weight to improve adhesion and to react the secondary hydrogen of the epoxy resin with the free isocyanate group of the urethane in Component (A). Suitable epoxy resins include bisphenol A epoxy, bisphenol F epoxy, bisphenol S epoxy and mixtures thereof. The molecular weight of epoxy resin is preferred to be less than 2000, because a high molecular weight epoxy makes the formulation too viscous for application. The preferred epoxy is bisphenol A epoxy.

7) Polyol

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An optional polyol may be added in an amount of from 1 to 10%, by weight, in order to react with any residual isocyanates from the urethane in Component (A). A polyol has the formula HO - R - OH where R may be aromatic or aliphatic, preferably having 1 to 10 carbons. Aliphatic polyols are most preferred for

high reactivity. Polyols having more than 4 carbons are particularly preferred. Suitable polyols include butanediol, hexanediol, ethylene glycol, tetraethylene glycol, and mixtures thereof.

5 8) Acrylate epoxy urethane

An acrylate epoxy urethane may be optionally added in an amount of from 5 to 80% by weight in order to improve adhesion, hardness and toughness characteristics of the composition.

10 The acrylated epoxy urethane may be prepared using an epoxy resin such as a bisphenol epoxy resin which a bisphenol A epoxy resin, a bisphenol F epoxy resin, or a bisphenol S epoxy resin include, as these epoxy resins promote adhesion of the coating to the surface. A bisphenol A epoxy resin is most preferred because it is less expensive. The epoxy resin should also be soluble in a liquid acrylate, which is used as a solvent for the reactants. The liquid acrylate is later reacted into the coating. Examples of suitable liquid acrylates include phenol ethoxylate monoacrylate, tetrahydrofurfuryl methacrylate, cyclohexyl methacrylate, 15 n-hexyl methacrylate, 2-(2-ethoxy ethoxy) ethyl acrylate, phenoxy ethyl acrylate (PEA) and mixtures thereof. The preferred liquid acrylate is phenoxy ethyl acrylate (PEA). Sufficient liquid acrylate of from 10 to 50% (by weight) should be used to give the resin a workable viscosity.

20 An epoxy catalyst, a tertiary amine, such as triethylamine, triethanolamine, benzyldimethylamine, and mixtures thereof, is also included in the resin. Generally, at least from 0.01% (all percentages herein are by weight unless otherwise indicated) catalyst (based on the weight of copolymer) is required, and more than 0.1% catalyst should be avoided as it causes the polymer to gel and may result in clouding.

25 A dual functional acrylate monomer or reactant is used to react with epoxy to obtain an acrylate epoxy urethane oligomer. Isocyanato ethyl methacrylate manufactured by Norquay Technology Inc., Chester, PA, is a preferred monomer. The dual functional reactant may also be prepared by reacting one mole of hydroxy terminated acrylate, such as hydroxy ethyl acrylate, with one mole of diisocyanate such as toluene diisocyanate. Other Examples of suitable hydroxy acrylates has been described in Component (A). The hydroxy ethyl acrylate is preferred because of its high reactivity. Other aliphatic and aromatic diisocyanates also can be used to make acrylate isocyanate monomer. These isocyanates have been described hereinabove in Component (A).

30 The acrylated epoxy urethane oligomer is usually obtained by reacting one mole of epoxy resin with one mole acrylate isocyanate monomer. The molar ratio range of epoxy to acrylate isocyanate is from 1:1 to 1:5. If the ratio is less than 1:1, the curing rate may be too slow and if the ratio is higher than 1:5, the coating may be too brittle.

35 Table 1 describes certain presently preferred resin compositions of the compositions of the present invention.

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Table 1
Resin Composition for UV-Moisture-Anaerobe Conformal Coatings

Resin	Composition Mole/Component
10035	1/HEA, 1/TDI
12524	1/HEA-TMA, 2/Epon 1004; in 50% PEA
10736	1/HEA-TMA, 2/Epon 1007; in 50% PEA
12061	1/Epon 1004, 1/IEM; in 50% PEA
11608	1/HEA, 1/TDI, 1/Caprolactam; in 20% PEA
BBM4-31	3/MCHDI, 1/PTMG 1000
*HEA:	Hydroxy ethyl acrylate
TDI:	Toluene diisocyanate
TMA:	Trimellitic anhydride
Epon 1004:	Bisphenol A epoxy with epoxy equivalent 875
Epon 1007:	Bisphenol A epoxy with epoxy equivalent 2250
PEA:	Phenoxy ethyl acrylate
IEM:	Isocyanate ethyl methacrylate
PTMG 1000:	Polyoxytetra methylene glycol with molecular weight 1000
MCHDI:	4,4'-methylene-bis (cyclohexyl isocyanate)

Table 2 illustrates examples of Component (A) compositions. Table 3 illustrates examples of Component (B) compositions.

Table 2
Composition of First Part of UV-Moisture-Anaerobe Curable Conformal Coatings

Formulation #	10035	10035-1	% Weight Composition* 10736	BM4-31	TDI	PEA	HDDA	IRG651	FC-171
SC-1#	96.15	—	—	—	—	—	—	3.85	—
SC-2#	—	96.15	—	—	—	—	—	3.85	—
SC-3#	76.92	—	—	—	—	9.61	9.61	3.85	—
SC-4#	76.92	—	—	—	19.23	—	—	3.85	—
SC-5	—	—	—	—	19.10	—	72.90	8.00	—
SC-6	—	—	—	—	19.10	—	72.90	8.00	0.10
SC-7	—	—	—	—	19.10	—	72.90	8.00	0.10
SC-8	—	—	—	—	19.10	—	72.90	8.00	0.10
SC-9	50.00	—	—	—	—	50.00	—	—	—
SC-10	50.00	—	—	—	—	50.00	—	—	—
SC-11	50.00	—	—	—	—	50.00	—	—	—
SC-12	50.00	—	—	—	—	50.00	—	—	—
SC-13	48.00	—	—	—	—	48.00	—	4.00	—
SC-14	48.00	—	—	—	—	48.00	—	4.00	—
SC-15	—	100.00	—	—	—	—	—	—	—
SC-16	—	100.00	—	—	—	—	—	—	—
SC-17	—	—	—	75.13	—	24.87	—	—	—

*10035: Acrylate urethane with free isocyanate
10035-1: Acrylate urethane with free isocyanate

10736: Acrylate epoxy

BM4-31: Urethane with free isocyanate

TDI: Toluene diisocyanate

PEA: Phenoxyl ethyl acrylate

HDDA: Hexanediol diacrylate

IRG 651: 2,2-dimethoxy-2-phenyl acetophenone

FC-171: Fluorohydrocarbon, 3M

#SC-1, SC-2, SC-3, SC-4 are single component moisture curable urethane coatings.

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Table 3
Compositions of Second Part of UV-Moisture Anacero Curable Conformal Coatings

Formulation	EPON1004	EPON1007	12524	12061	11608	10736	Butanediol	IRA	EPMA	PEA	EDDA	TEGDA	IRG651	FC-171	Acrylic Acid
SC-5	50.00	---	---	---	---	---	---	12.72	---	37.28	---	---	---	---	---
SC-6	50.00	---	---	---	---	---	---	12.72	---	37.28	---	---	---	---	---
SC-7	43.86	6.14	---	---	---	---	---	12.72	---	37.28	---	---	---	---	---
SC-8	---	---	76.54	---	---	10.75	5.06	20.52	---	34.87	32.00	---	6.51	0.10	---
SC-9	---	---	---	---	---	---	---	20.52	---	34.87	32.00	---	6.51	0.10	---
SC-10	5.06	---	---	---	---	---	---	21.22	---	---	33.12	---	6.75	0.23	---
SC-11	---	---	---	38.71	---	---	---	21.22	---	---	33.12	---	6.75	0.23	---
SC-12	---	---	---	---	---	38.71	---	---	24.81	25.84	10.88	3.08	2.81	0.27	---
SC-13	---	---	---	---	3.21	28.70	---	---	12.50	30.08	12.67	4.63	3.27	0.27	---
SC-14	---	---	---	---	3.74	33.40	---	---	31.87	11.06	38.93	11.06	6.64	0.22	5.53
SC-15	---	---	---	---	---	---	---	---	31.87	11.06	33.62	11.06	6.64	0.22	5.53
SC-16	---	---	---	---	---	---	---	---	25.06	8.70	26.44	8.70	5.22	0.17	4.35
SC-17	---	---	---	---	---	21.37	---	---	---	---	---	---	---	---	---

*EPON 1004: Bisphenol A epoxy with epoxy equivalent weight 875

EPON 1007: Bisphenol A epoxy with epoxy equivalent weight 2250

12524: Acrylate epoxy

11608: Acrylate urethane

12061: Acrylate epoxy

10736: Acrylate epoxy

IRA: Hydroxy ethyl acrylate

EPMA: Hydroxy propyl methacrylate

PEA: Phenoxyl ethyl acrylate

EDDA: Hexanediol diacrylate

TEGDA: Tetraethylene glycol diacrylate

IRG651: 2,2-dimethoxy-2-phenyl acetophenone

FC-171: Fluorohydrocarbon, 3M

Table 4 summarizes the final composition after components (A) and (B) are mixed.

Each component has a shelf life greater than 3 months. The mixture of components (A) and (B) has a workable low viscosity in the range of 200 to 300 cps over an 8 hour period at room temperature, so the coating can be easily sprayed, dip coated, or knife coated on the substrate. The coatings can be cured upon UV exposure. While not wishing to be bound by theory, it is believed that in the shadow areas, the urethane having the free isocyanate group in the coating reacts with moisture from the atmosphere first to generate carbon dioxide which creates a localized anaerobic environment, so the acrylates in the coating are subsequently cured anaerobically. These new conformal coating compositions exhibit good performance as shown in Tables 5 and 6. The properties of cure rate, moisture permeability and electric insulation are better than that of commercially available UV two-component conformal coatings.

The invention will now be illustrated with reference to the following examples.

EXAMPLES

Preparation of two-component conformal coating

Formulation I (SC-13)

Preparation of Component A	
Ingredients	Amount (grams)
Hydroxy ethyl acrylate (HEA)	696
Toluene diisocyanate (TDI)	1044
Benzoquinone (BQ)	1.8
Phenoxy ethyl acrylate (PEA)	884.4
UV photoinitiator 2,2-dimethoxy-2-phenyl-acetophenone (Irg 651)	104.5

Reaction Procedures:

A 5 liter flask is prepared having a thermometer, stirrer, nitrogen sparge or dry air (min.), and a water condenser. TDI is added to the flask. BQ is dissolved in HEA and the mixture is added into the TDI gradually and slowly. The temperature should remain below about 60°C while adding the mixture into flask. The mixture is reacted at 60°C for about one hour, then PEA and Irg 651 are added and mixed well for about 30 min. The viscosity of the resin at 25°C should be about 200 cps/25°C. The resin should be stored preferably under dry air or dry nitrogen in an air-tight amber plastic bottle and kept away from moisture.

Preparation of Component (B)	
Ingredients	Amount (grams)
Epon 1007F (Bisphenol A Epoxy)	139.6
Phenoxy ethyl acrylate (PEA)	130
Adduct of hydroxy ethyl acrylate (HEA) and trimellitic anhydride (TMA)	4.7
Triethanolamine (TEA)/PEA	0.085 TEA in 12.6 PEA
Acrylate urethane in PEA	290.5
Tetraethyleneglycol diacrylate (TEGDA)	39.8
Hexanedioldiacrylate (HDDA)	108.8
Hydroxy propyl methacrylate (HPMA)*	248
UV photoinitiator 2,2-dimethoxy-2 phenyl-acetophenone (Irg 651)	28.1
Flow control agent fluoro-hydrocarbon (FC-171)	1.9
*HPMA - Rohm and Haas Rocryl 410	

Reaction Procedures:

A 2-3 liter flask is prepared having a stirrer, nitrogen or dry air sparge (min), water condenser and thermometer. Epon 1007F is dissolved in PEA at about 100° C. The adduct of HEA and TMA and TEA in PEA are added into the flask and heated to about 140-150° C. The mixture is reacted at about 140-150° C for about 1.5 hours and until the acid number is below 5. The mixture is cooled to about 80° C. The acrylate urethane in PEA, TEGDA, HDDA, HPMA, Irg 651 and FC-171 are added and mixed well for about a half hour. The viscosity of the reaction mixture is measured at 25° C and is preferably about 200 cps. The resin is stored under dry air (preferred) or nitrogen in an air-tight amber plastic bottle and kept away from moisture.

The preparation of the adduct of hydroxy ethyl acrylate (HEA) and trimellitic anhydride (TMA)	
	Amount (grams)
Hydroxy ethyl acrylate (HEA)	403
Benzoquinone (BQ)	9.3
Trimellitic anhydride (TMA)	666.8

Reaction Procedures:

A 2-3 liter flask having a stirrer, nitrogen sparge (min), water condenser and thermometer is prepared. HEA and BQ are added into the flask and the temperature is set at about 100° C. TMA is added portionwise over about a half hour period. The mixture is reacted at about 150° C for about one hour. The resin is drained while it is hot in an aluminum pan and broken into small pieces before the preparation of Component (B).

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Preparation of acrylate urethane in PEA	
Ingredients	Amount (grams)
Toluene diisocyanate (TDI)	34.82
Benzoquinone (BQ)	0.012
Hydroxy ethyl acrylate (HEA)	23.22
Caprolactam	22.62
Phenoxy ethyl acrylate (PEA)	834.29

Reaction Procedures:

A 2-3 liter flask is prepared having stirrer, thermometer, dry nitrogen or air sparge (min), and water condenser. TDI is added into the flask. HEA and BQ are mixed and added into the TDI gradually and slowly. The exotherm temperature should be kept below about 60° C. The mixture is reacted at about 60° C for about one hour. The caprolactam is added and reacted at about 100° C for about one hour. PEA is added and mixed well for about a half hour.

Preparation of Formulation I (SC-13) Conformal Coating

Mix equal parts (by weight) of Components A and B together well before application. The mixture should be used in about 8 hours.

Formulation II (SC-14)

Preparation of Components (A) and (B)

The preparation procedures are the same as Formulation I except the amount of each ingredient of Component B is different and shown in the following:
Component (A) is the same as Component (A) of Formulation I.

Component (B)	
Ingredients	Amount (grams)
Bisphenol A (Epon 1007F)	162.46
Phenoxy ethyl acrylate (PEA)	151.29
Adduct of PEA and TMA	5.47
Triethanolamine (TEA)/PEA	0.01 TEA in 14.7 PEA
Acrylate urethane in PEA	338.2
Tetraethyleneglycol diacrylate (TEGDA)	46.3
Hexanedioldiacrylate (HDDA)	126.7
Hydroxy propyl methacrylate (HPMA)*	125
UV Photoinitiator (2,2-dimethoxy-2-phenyl-acetophenone (Irg 651)	32.7
Flow control agent fluoro-hydrocarbon (FC-171)	1.9

*HPMA Rohm and Haas Rocryl 410.

The viscosity of Component B of Formulation II is about 350 cps/25° C.

Preparation of Formulation II Conformal Coating

Mix one part (by weight) of Component (A) and two parts of Component (B) together well before application and use the mixture in about 8 hours.

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Table 4

FINAL COMPOSITION OF CONFORMAL COATING AFTER MIXING PART 1 AND PART 2

FORMULATION	10035	10035-1	RB144-31	EPON1004	EPON1007	12524	12061	10736	11608 BUTANEDOL	1EA	14PMA	PEA	14ODA	TEEDA	ARG651	FC171	ACRYLIC/ACD	TDI
SC-1	86.15	-	-	-	-	-	-	-	-	-	-	-	-	-	3.85	-	-	-
SC-2	-	96.15	-	-	-	-	-	-	-	-	-	-	-	-	3.85	-	-	-
SC-3	76.92	-	-	-	-	-	-	-	-	-	-	0.61	0.61	-	3.85	-	-	-
SC-4	76.92	-	-	-	-	-	-	-	-	-	-	-	-	-	3.85	-	-	18.23
SC-5	-	-	-	25.00	-	-	-	-	-	6.36	-	18.64	36.45	-	4.00	-	-	9.55
SC-6	-	-	-	25.00	-	-	-	-	-	6.36	-	18.64	36.45	-	4.00	0.01	-	9.55
SC-7	-	-	-	21.93	3.07	-	-	-	-	6.36	-	18.64	36.45	-	4.00	0.05	-	9.55
SC-8	-	-	-	-	-	30.27	-	5.38	-	6.36	-	-	36.45	-	4.00	0.05	-	9.55
SC-9	25.00	-	-	-	-	-	-	-	2.98	10.26	-	42.44	16.00	-	3.25	0.10	-	-
SC-10	25.00	-	-	2.98	-	-	-	-	-	10.26	-	42.44	16.00	-	3.25	0.10	-	-
SC-11	25.00	-	-	-	-	19.35	-	-	-	10.61	-	25.00	16.56	-	3.25	0.12	-	-
SC-12	25.00	-	-	-	-	-	-	19.36	-	10.61	-	25.00	18.78	-	3.32	0.12	-	-
SC-13	23.75	-	-	-	-	-	-	14.52	1.62	-	12.55	36.02	5.51	2.01	3.31	0.13	-	-
SC-14	15.86	-	-	-	-	-	-	22.36	2.50	-	0.37	36.00	8.48	3.10	3.49	0.14	-	-
SC-15	-	-	50.00	-	-	-	-	-	-	-	15.94	5.53	19.47	5.53	3.32	-	-	-
SC-16	-	-	50.00	-	-	-	-	-	-	-	15.94	5.53	16.01	5.53	3.32	0.11	2.77	-
SC-17	-	-	27.36	-	-	-	-	13.59	-	-	15.94	14.58	16.81	5.53	3.32	0.11	2.77	-

*All the formulations were mixed by one part (wt) of Part 1 and one part of Part 2 except SC-14, was mixed by one part of Part 1 and two parts of Part 2 and SC-17 was mixed by one part of Part 1 and 1.75 parts of Part 2.

Table 5

5	Adhesion and Hardness of Two Component Conformal Coatings						
10		Cross Hatch Adhesion		Pencil Hardness		Heat Shock	
		(% ASTM D3359)		(ASTM D3363)		1/8" Mandrel bend	
	Formulation	FR-4	Tin	FR-4	Tin	150 ° C/0.5 hr	Comment
15	SC-1	0	0	--	--	0.5	Very brittle coating
	SC-2	0	0	--	--	---	Very brittle coating
	SC-3	0	0	3H	--	----	Very brittle coating
	SC-4	0	0	3H	--	----	Very brittle coating
20	SC-5	100	97	3H	3H	----	Good coating
	SC-6	100	100	2H	--	Pass	Good coating
	SC-7	100	0	3H	2H	Fail	Poor adhesion on tin
	SC-8	100	0	3H	F	Fail	Poor adhesion on tin
25	SC-9	100	0	3H	2H	----	Poor adhesion on tin
	SC-10	100	0	3H	2H	----	Poor adhesion on tin
	SC-11	100	0	3H	2H	----	Poor adhesion on tin
	SC-12	100	0	3H	2H	----	Poor adhesion on tin
30	SC-13	100	100	3H	2H	Pass	Good coating
	SC-14	100	100	3H	2H	Pass	Good coating
	SC-15	---	100	--	HB	----	Slow cure, need double exposure poor stability
	SC-16	---	75	--	HB	Pass	Viscosity too high
	SC-17	---	100	--	H	Fail	Viscosity too high

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Table 6

Properties of Two-Component Conformal Coatings				
Properties	SC-6	SC-13	SC-14	Loctite 361
Solvent in system	No	No	No	Yes
Pot life (hours)	8	8	8	8
No. of component	2	2	2	2
Viscosity (cps/25° C)	200	200-300	200-300	70
Cure schedule				
Exposed to UV light (sec)	2-4	2-4	2-4	overnight
Shadow area (day)	3	3	3	3
Dielectric constant (25° C, 1MHz, ASTM D2305)	3.3	3.1	3.3	3.9
Dissipation factor (25° C, 1MHz, ASTM D2305)	0.0280	0.0249	0.0289	0.0570
Dielectric Strength (V/mil) (ASTM D149, 2 mil film)	2592	2349	2839	1917
Volume resistivity (ohm-cm) (ASTM D257)	3.4×10^{14}	7.2×10^{15}	4.8×10^{15}	1.1×10^{13}
Surface resistivity (ohm/sq) (ASTM D257)	3.0×10^{14}	9.2×10^{16}	1.7×10^{17}	8.1×10^{12}
Flexibility (Mil-1-46058C)	Pass	Pass	Pass	Pass
Specific permeability (mg/cm ² day, ASTM D1653)	0.3174	0.2488	0.1717	----
Cross hatch adhesion (%) (ASTM D3359)				
	Tin	100	100	100
	FR-4	100	100	100
Linear TEC (° C ⁻¹)		3.28×10^{-4}	2.08×10^{-4}	3.009×10^{-4}
Glass Transition Temp.(T _g ° C)	60	38	43	17

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by reaction of said urethane with caprolactam; (3) reactive diluents; (4) UV photoinitiators; and (5) additives; and

(C) mixing components (A) and (B).

13. The composition according to claim 4 characterised in that the epoxy resin is a bisphenol epoxy.

5 14. The composition according to claim 5 characterised in that the polyol is an aliphatic having 1 to 10 carbons or aromatic.

15. The composition according to claim 6 characterised in that the acrylate epoxy urethane is the reaction product of a bisphenol epoxy and isocyanato ethyl methacrylate.

10 16. The composition according to claim 1 characterised in that Component (A) and Component (B) are present in about equal parts by weight.

17. The composition according to claim 1 characterised in that Component (A) and Component (B) are present in about a 1 to 2 ratio, by weight.

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It will be appreciated that the above-described invention provides a UV curable conformal coating composition with low moisture permeability, a quick cure, good electrical insulating properties, and shadow cure capabilities. The problem of ineffective cure of the shadow areas is eliminated by the composition of the present invention. This composition may be applied by spray, dipping or knife coating and cured by UV in a short time. The conformal coating of the present invention is, especially useful in automated printed wiring board assembly lines.

Whereas particular embodiments of the invention have been described above for purposes of illustration, it will be appreciated by those skilled in the art that numerous variations of the details may be made without departing from the invention as described in the appended claims.

Claims

1. An ultraviolet radiation curable composition characterised in that said composition comprises a mixture

Component (A) which comprises a mixture of (1) from 40 to 80% by weight, of a urethane having a free isocyanate group; (2) from 20 to 60% by weight of reactive acrylate diluents; (3) from 0 to about 10% by weight, of UV photoinitiators; (4) from 0 to 10%, by weight, of additives; and

a mixture of Component (B) which comprises (1) from 5 to 80% by weight, based on total composition weight, of an acrylate-epoxy resin which comprises an unsaturated epoxy oligomer having a molecular weight of from 2000 to 5000, where the epoxy in said oligomer is a bisphenol epoxy; (2) from 1 to 10% by weight, based on total composition weight, of an acrylate-urethane oligomer; (3) from 10 to 94% by weight of reactive acrylate monomers; (4) from 0 to 10%, by weight, of UV photoinitiators; and (5) from 0 to 10%, by weight, of additives, with the proviso that the total percentage weight of said UV photoinitiators and additives respectively each not be less than 1 percent and not exceed about 10 percent.

2. The composition according to claim 1 characterised in that Component (A) includes from 1 to 25%, by weight of polyisocyanate monomers.

3. The composition according to claim 1 characterised in that the reactive acrylate monomers are selected from the group consisting of acrylate monomers having a hydroxy functional group, resin soluble acrylate monomers, acrylate monomers having low moisture permeability, acrylate monomers having an ether linkage, and mixtures thereof.

4. The composition according to claim 1 characterised in that Component (B) includes about 5 to 80%, by weight, of an epoxy resin.

5. The composition according to claim 1 characterised in that Component (B) includes about 1 to 10%, by weight, of a polyol.

6. The composition according to claim 1 characterised in that Component (B) includes about 5 to 80%, by weight, of an acrylate epoxy urethane.

7. The composition according to claim 3 characterised in that the reactive acrylate monomers include about 10 to 50%, by weight, of an acrylate monomer having a hydroxy functional group, a resin soluble acrylate monomer or an acrylate having low moisture permeability.

8. The composition according to claim 3 characterised in that the reactive acrylate monomers include about 1 to 15% by weight, of an acrylate monomer having ether linkages.

9. The composition according to claim 1 characterised in that Component (A) reactive acrylate diluents are free of active hydrogen groups.

10. The composition according to claim 9 characterised in that the reactive acrylate diluents are monoacrylate monomers or diacrylate monomers.

11. The composition according to claim 7 characterised in that the acrylate monomer having a hydroxy functional group is selected from the group consisting of hydroxy ethyl acrylate, 3-hydroxy propyl acrylate, 2-hydroxymethacrylate, hydroxy-beta-carboxy ethyl acrylate, 3-hydroxy propyl 2-hydroxy propyl acrylate, 2-hydroxy ethyl methacrylate, methacrylate, and mixtures thereof.

12. A method of making a UV curable composition comprising:

(A) preparing a urethane having a free isocyanate group by reacting polyols or alcohols with one stoichiometric equivalent of excess polyisocyanate, adding a reactive acrylate diluent, and a UV photoinitiator;

(B) preparing a mixture of (1) an acrylate epoxy monomer which is prepared by reacting an anhydride or a diacid with a hydroxy acrylate followed by reaction with a bisphenol epoxy; (2) an acrylate-urethane monomer prepared by reacting a diisocyanate with a hydroxy acrylate to form a urethane, followed



European Patent
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EUROPEAN SEARCH REPORT

Application number

EP 90302197.0

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.)
D, A	<u>US - A - 4 424 252</u> (NATIVI) * Claims * --	1	C 09 D 175/04 C 09 D 163/10// (C 09 D 163/10 C 09 D 175:14) C 08 F 2/48
A	<u>US - A - 4 533 975</u> (BILL) * Claims * --	1	
A	<u>EP - A1 - 0 044 150</u> (WESTINGHOUSE ELECTRIC CORPORATION) * Claims * -----	1	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.)
			C 09 D C 08 F
Place of search VIENNA		Date of completion of the search 31-05-1990	Examiner PAMMINGER

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